Radicals and Oxidants Instrument (ROXI) for Mars surface analyses

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ABSTRACT

Electron Paramagnetic Resonance (EPR) spectroscopy is likely the most sensitive technique for detection of elements and compounds with unpaired electrons. Typical analyses in the laboratory utilize a fixed microwave frequency and a scanning magnetic field to induce electron spin-state transitions in the sample. The location of the resonant absorption in the scan is a diagnostic property of the material, and the intensity of the signal is proportional to the concentration. We have developed a frequency scan EPR for planetary surface applications where a fixed magnetic field and tunable microwave sources are used to produce these characteristic resonant peaks. Our narrowband spectrometer covers 7.5 to 8.5 GHz at a field strength 2.8 kGauss and is specifically designed for the identification of organic radicals, minerals with radiation-induced defects, and reactive compounds in martian surface samples. Our wideband spectrometer covers 2.0 to 8.0 GHz at a field strength of 1.0 kGauss and is useful for the detection of paramagnetic cations. The detection limit of the narrowband and wideband spectrometers for species with unpaired electrons is 50 PPB and 1 PPM, respectively.

Keywords: Mars, electron paramagnetic resonance

1. INTRODUCTION

Electron Paramagnetic Resonance (EPR), also know as Electron Spin Resonance (ESR), spectroscopy is an extremely sensitive technique used in the study of atoms and molecules with unpaired electrons. This method of analysis was discovered in 1944 when E. K. Zavoisky at Kazan University observed that copper salts placed in a magnetic field absorbed microwave radiation in a narrow frequency band. This result was later explained by spin-state transitions of electrons in the sample. The specific combination of magnetic flux density and microwave frequency of the resonant absorption is a unique feature of each compound with unpaired electrons. Since its discovery, the technique of EPR spectroscopy has been successfully applied in the detection, identification, and quantification of oxidizing compounds, organic radicals, radiation-induced defects, and transition metal cations [e.g., Weil et al., 1994].

In most molecules, electrons are paired, resulting in magnetic moments that are equal and opposite. However, unpaired electrons can exist in atoms and molecules through extraction or addition of a single electron by an oxidation/reduction process or through energetic processes that damage crystal structures and leave defect centers. These "paramagnetic" entities have permanent magnetic dipole moments due to uncompensated electron spin, and when placed in a magnetic field the unpaired electrons will align either parallel or antiparallel to the field. The unpaired electron can be made to transition between the two states (Zeeman energy levels) by absorption of energy from microwave photons. When the energy associated with the frequency of microwave stimulation matches the energy difference between the Zeeman levels (resonance), energy absorption takes place and this is detected by EPR.

By recording the frequency (ν) and applied magnetic field ($\underline{H}$) where the resonance occurs, the g-values of the spectra can be determined ($g = h\nu/\beta\underline{H}$, where h = Plank's constant; β = Bohr magneton). These g-values, along with the line width and shape of the resonance, are diagnostic characteristics of the paramagnetic species and are used to determine which radicals, defect centers, or cations are responsible for the signal. In addition to identification of the paramagnetic species with high specificity, the concentrations can also be determined from the areas bounded by the resonance features.

EPR spectroscopy is likely the most sensitive technique for direct characterization of atoms and molecules with unpaired electrons. Detection limits achievable in the laboratory are better than 10^{11} unpaired electron spins per cubic centimeter of sample. Analyses can be conducted with minimal sample preparation under ambient environmental conditions using samples of only a few milligrams.

2. SCIENCE

The Radicals and Oxidants Instrument (ROXI) for Mars surface analyses has four major science objectives:

Understand the oxidants responsible for the unusual reactivity of the martian soil and determine their effects on organic molecules.

Detect and identify organic radicals that may be present at the martian surface.

Characterize the surface radiation environment and identify radiation-damaged mineral phases.

Quantify the abundance of paramagnetic cations in the martian surface environment.

2.1 Martian Oxidants

The Viking Lander biology experiments indicate that highly reactive oxidizing species which actively destroy primitive and meteoritic organic molecules are present at the surface of Mars. The specific observations are as follows:

- The Gas Chromatograph/Mass Spectrometer (GCMS) revealed that martian soil was free of detectable organic material, despite significant meteoritic infall [Biemann et al., 1977].
- The Gas Exchange (GEx) investigation team discovered that humidification of the soil released excess oxygen even after heating to 145ºC [Oyama and Berdahl, 1977], suggesting the presence of a strong, thermally-stable compound capable of oxidizing water [Klein 1977].
- The Labeled Release (LR) investigation determined that ^{14}C-labeled nutrient solutions were decomposed upon contact with the soil [Levin and Straat, 1977].

Based upon the quantity of oxygen released in the GEx and the decomposition of organic nutrients in the LR, the predicted concentration of reactive compounds is on the order of 1 to 35 parts-per-million [McKay et al., 1998]. The composition of the reactive phases, mechanisms of formation, and interactions with organic compounds have not yet been determined. In order to be consistent with the Viking data, the putative oxidants must be stable at the martian surface, must exist at a depth of approximately 10 cm (subsurface Viking samples were reactive), and must have a plausible formation mechanism.

Hydrogen peroxide, as a precipitate of atmospheric photochemistry, is often discussed as a likely oxidant at the surface of Mars [e.g., Hunten, 1979; Oro and Holtzer, 1979]. H_2O_2 is capable of decomposing organic compounds, but in the presence of transition metal oxides (abundant in martian surface minerals), it decomposes into active oxygen species, such as O^-, O_2^- and O_3^- which could remain on the surface of mineral grains [Antcliff et al., 2003].

These oxygen compounds are paramagnetic and are directly detectable with ROXI. Active oxygen species may also form directly on the surface of mineral grains as a result of exposure to ultraviolet radiation in the presence of atmospheric oxygen [Yen et al., 2000]. In this process, UV photons transmitted through the martian atmosphere mobilize electrons within the substrate that migrate to surface sites where they are subsequently captured by gas phase oxygen resulting in adsorbates such as O_2^- [Ito et al., 1985].

In addition to hydrogen peroxide and oxygen radicals, a number of other candidate martian oxidants have been proposed. Reactions involving oxidizing species will typically involve formation of paramagnetic entities, because the processes involve single electron transfer from one molecule to another. ROXI can detect and quantify oxidants present at the surface of Mars in concentrations greater than 50 ppb either directly or through measurements of the reaction products.

2.2 Organic Radicals

Given the results of the Viking Landers which show the presence of unknown oxidizing agents in analyzed soils, it has been generally assumed that organic matter that reaches the modern martian surface is oxidized to carbon dioxide or other volatile organic compounds on geologically short time scales. There are, however, uncertainties associated with this interpretation of the Viking GCMS data. Macromolecular organic carbon is often quite refractory, and does not

always volatilize at typical pyrolysis temperatures of up to 500ºC. The Viking GCMS carried out pyrolysis at temperatures at or below 500ºC [Biemann et al. 1977] and may not have detected all types of organic macromolecules present in the analyzed regolith samples, particularly stable partial oxidation products [Benner et al., 2000].

Carbonaceous material that combusts in the 500-600ºC range, and appears from ^{14}C data to be extraterrestrial, has been detected at low concentrations in the martian meteorite ALH84001 [Jull et al. 1998]. In addition, local temperature and water activity may affect the rates of oxidation of organic macromolecules, leading to oxidation lifetimes that are geologically significant [McDonald et al. 1998]. It is also possible that low-porosity rocks as well as certain mineral structures may protect embedded organics by limiting diffusion of volatile oxidants.

The bulk of organic material reaching the surface of Mars over its history, whether produced in situ by abiotic or biological processes or delivered to the surface by impactors, would most likely have been in the form of heteropolymeric macromolecules. The bulk of the organic carbon in carbonaceous chondrites, which can be assumed to have impacted the martian surface over its history, is in macromolecular form similar to kerogen [Hayatsu et al. 1977, 1980; Cronin et al. 1988]. In biological systems on Earth, half or more of the dry weight of a cell is represented by biomacromolecules such as proteins and nucleic acids [Darnell et al. 1990]. If present on Mars, these molecules could have been converted to complex organic materials such as humic substances and kerogens if buried in sediments [Hayes et al., 1983]. Such materials from Archean rocks and from carbonaceous meteorites have been shown to have trapped radicals detectable by EPR [Binet et al. 2004, Skrzypczak et al. 2004] (Figure 1).

Through the sensitizing effect of water molecules, trace quantities of other organic material can be effectively transformed to stable radicals and become detectable by EPR. By interaction with thin films of adsorbed H_2O or ice deposits in the martian regolith, high-energy radiation (e.g., from galactic cosmic rays) creates ·OH radicals. These products are sufficiently mobile at temperatures as low as 150K to diffuse through the matrix. Even though the majority of ·OH radicals decay by recombination processes, a minor fraction will interact with organic impurities and initiate a secondary reaction by transfer of unpaired electrons. ROXI will detect radicals produced through this mechanism with a sensitivity of better that 50 ppb and allow determination of the likely original molecular structures and their concentrations.

2.3 Radiation-Induced Defects

Ionizing radiation at the surface of Mars (galactic cosmic rays, solar protons, radioactive decay, etc.) damages mineral structures producing defect centers detectable with EPR. The radicals reflect the structure of the host matrix as well as specific chemical environments within the sample. For example, after γ-ray irradiation, electron hole centers such as CO_3^-, $CO_2(H)$, SO_4^-, NO_3^- were detected from matrices of carbonates, bicarbonates, sulfates, bisulfates and nitrates (Figure 2). The g-values and line widths of the spectral features can be uniquely correlated with the mineral phases in which the defects were detected. Thus, ROXI can examine the mineralogy of martian surface samples through characterization of the radiation damage centers.

The flux of galactic cosmic rays alone contributes approximately 0.02 rad/day to silicon at the surface of Mars [Farguson et al., 2003], where 1 rad represents a deposited energy of 0.01 Joules per kilogram of silicate rocks. Figure 3 shows the EPR signature of a natural clay sample after a total dose of 50 krad, equivalent to ~7000 years of cosmic ray exposure on Mars. In these spectra, we observe all three known defect centers from silicate minerals, namely, oxygen hole centers (OHC), peroxy centers, and E_1' centers. We can tell from the g-values and linewidths that quartz impurities are present in this particular sample. Samples at the surface of Mars will have cosmic ray exposure ages much greater than 7000 years, so observable radiation-induced damage centers are likely present.

Figure 4 shows that the EPR amplitude, which corresponds to the abundance of defect centers, begins to saturate after exposures of ~10^3 Gray (~100 krad). Assuming saturation after exposure for geologic timescales, the EPR signal intensity can be used to infer the mineral abundance as well as its composition. The detection limit for radiation defects in minerals is 50 ppb.
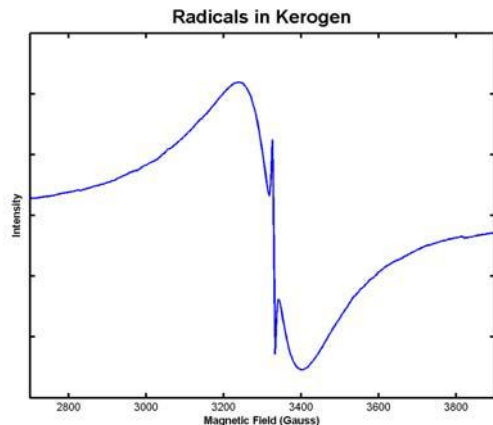
Figure 1: Trapped radicals in a kerogen sample. The spikes in the middle (g=2.0029) are characteristic of small H:C ratios in highly evolved organic compounds.
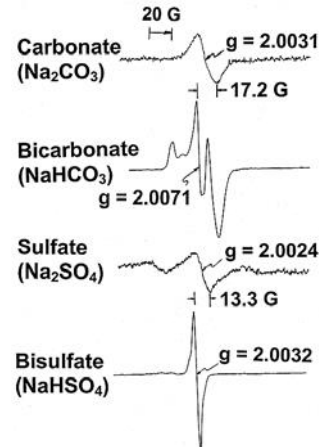

Figure 2: Defect centers in minerals. g-values and line widths uniquely establish the phase in which the defects are measured.
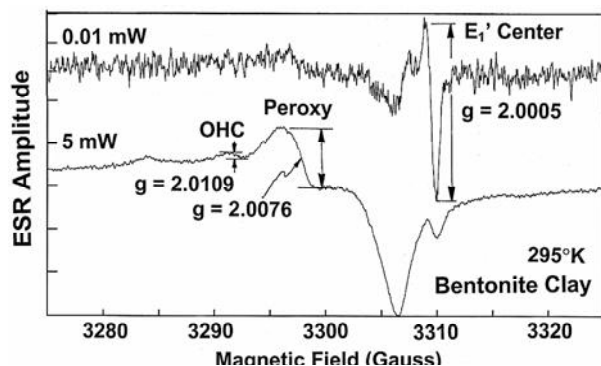

Figure 3: Spectra of defect centers produced in a clay mineral after a 50 krad exposure.
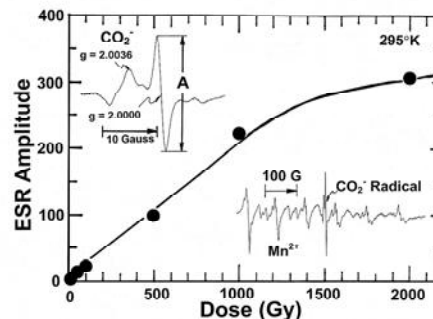

Figure 4: Sample relationship between total dose and signal intensity (1 Gy = 100 rad).

2.4 Paramagnetic Cations

Table I lists examples of elements and their oxidation states that are quantifiable with ROXI operating under Mars-ambient temperatures (1 ppm detection limit). Example spectra are shown in Figure 5.

Minor and trace element analyses of rocks and soils are useful for investigating their origins and weathering histories. ROXI will establish major oxidation states of key cations, including several (Cr, Mn, Ni) that have already been detected in martian soil and rocks using X-ray fluorescence but for which no information is currently available on their chemical form.

Samples with similar trace element fingerprints indicate that the source regions and/or weathering histories are related. Cation substitution (e.g., Mn^{2+} for Ca^{2+} in carbonates [Lloyd et al, 1993] or Cu^{2+}/V^{4+} for Al^{3+} in phyllosilicates [Goodman and Nadeau, 1990]) is controlled by the thermodynamics of formation or diagenesis. ROXI's ability to measure the abundance and oxidation states of minor and trace elements enables a detailed geologic study and correlation of collected samples.

The astrobiological significance of ROXI-detected elements is also high. Enzyme cofactors in a wide variety of organisms are provided by the essential trace elements: Mn, Fe, Co, Ni, Cu, and Mo. The latter element enables the greatest efficiency for nitrogenase, the essential enzyme for nitrogen fixation. Nitrogen appears to be the limiting nutrient for martian organisms since ammonia is not present in either the atmosphere or the soil, and any nitrates may have been scrubbed from the soil by acidic volcanic emissions. Not only will the presence of these elements be determined, but information on bioavailability may be possible via solubility inferences from their ionic states. Furthermore, biological partitioning of these elements could potentially be studied by measuring anomalous concentrations and gradients in these cations.

Table I: Cations measured by ROXI.

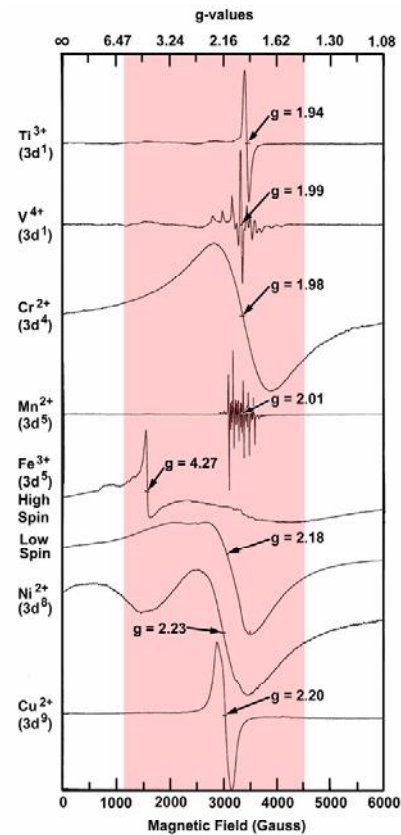| # of d-Electrons	Cations
1	Ti^{3+}, V^{4+}, Cr^{5+}, Mo^{5+}, Mn^{6+}
2	V^{3+}, Cr^{4+}
3	V^{2+}, Cr^{3+}, Mo^{3+}, Mn^{4+}
4	Cr^{2+}
5	Cr^{+}, Mn^{2+}, Fe^{3+}
7	Co^{2+}, Pd^{3+}, Ni^{3+}
8	Ni^{2+}
9	Cu^{2+}, Ag^{2+}

Figure 5: Example ion signatures. Shaded region ($1.43 < g < 5.72$) represents the ROXI scan range.

3. INSTRUMENT

The Radicals and Oxidants Instrument (ROXI) is designed for a Mars surface application on a platform such as a rover and consists of the following components:
  - Narrowband EPR spectrometer for characterizing reactive species, organic radicals, and radiation-induced defects.
  - Wideband EPR spectrometer for characterizing paramagnetic cations.
  - Thermal control subsystem, including a 250°C oven for annealing radiation-induced defects and replicating the thermal history of samples analyzed by Viking.
  - Calibration standards for the EPR spectrometers to allow in-flight determination of system performance.
  - Sample handling subsystem which moves 50 to 100 mg samples from the spacecraft (rover) delivery system to the spectrometers, oven, and dumping station.
  - Electronics and software for controlling the instrument and for interfacing with the rover.

3.1 Electron Paramagnetic Resonance Spectrometers

EPR spectra can be obtained either by scanning the magnetic field at a fixed microwave frequency (conventional laboratory instrument), or by scanning the microwave frequency at a fixed magnetic field. The latter method is more compatible with a compact, low power, low mass spectrometer. ROXI utilizes two sets of permanent magnets and tunable microwave resonators for the frequency scans, one set each for the narrowband and wideband EPR spectrometers.

The narrowband EPR scans a frequency range of 7.5 to 8.5 GHz and uses a 0.28 Tesla permanent magnet. This range covers g-values between 1.91 and 2.16, which is adequate for the detection of adsorbed radicals, organic radicals, and bulk defect centers. (The g-values of all radical species will be close to the free electron g value of 2.0023, centered at 7.85 GHz @ 0.28 Tesla). This frequency scan range corresponds to a 350 Gauss field scan in a conventional fixed frequency EPR spectrometer. Scanning of the resonator is accomplished using a small DC motor

The narrowband spectrometer has a detection capability of ∼ 10^{12} spins/cm^3 over its scan range and a quality factor, Q (a measure of the efficiency of the resonator), of 3000. These values compare well against a typical laboratory spectrometer with a detection capability of ∼ 10^{11} spins/cm^3 over a 6000 Gauss range and a Q of 5000.

Redox sensitive transition elements will be detected using a wideband EPR spectrometer (2 to 8 GHz at 1 kGauss, 1.43<g<5.72). Frequency scanning of the microwave signal is accomplished with a loop-gap resonator (LGR) in combination with a mechanical slider to produce the desired resonance frequency. The LGR can be viewed as a series of tuned resonance circuits whose frequency, ν, depends on the inductance, L, of the conductive cylinder (the loop) and the capacitance, C, of the gap: $\nu = 1/(2\pi(LC)^{1/2})$. A feedback circuit in the signal processing chain provides automatic frequency locking of the microwave source. The quality factor (Q) of this resonator is ∼300.

Figure 6 shows our fully functional, self-contained field unit that integrates the resonator, tuner, magnet, microwave source (voltage controlled oscillator, VCO), detection circuitry, batteries, and data acquisition computer. Numerous sample spectra (e.g., Figure 7) have been obtained with this hardware.

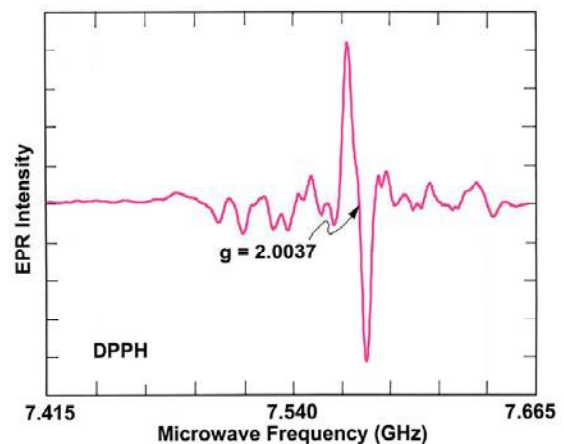**Figure 6**: Frequency scan field test unit (7.5 to 8.5 GHz, 1 W, 1.7 kg including batteries).

Figure 7: Frequency scan EPR data from the ROXI integrated prototype.

3.2 Sample Heating

The oven is designed to heat samples to temperatures up to 250ºC and to hold this temperature for a specified time (typically, 1 hour). These elevated temperatures will be used for testing the thermal stability of radiation-induced defects and for replicating the thermal protocols of the Viking Lander experiments. Samples will be allowed to cool to ambient temperatures prior to EPR measurements. The insulated oven will be 10 mm diameter and 30 mm deep to accommodate the sample holder. This oven will use standard electric heaters, with electronic control to provide the desired temperature levels.

3.3 Calibration Standard

A small sample of Mn^{2+} will be carried for calibration of both the narrowband and the wideband EPR spectrometers. This standard (embedded in the sample arm) is introduced to the spectrometers by the sample handling system and will be scanned before and after each analysis of a martian sample. Line positions and line widths will be used to verify the frequency scaling of the scans, and peak intensities will be used to track instrument performance.

4. DATA ANALYSIS

The EPR spectra from martian surface materials will be a superposition of all detectable compounds within the range of the scan. Determining the identity and the concentration of the constituents involves calculation of g-values, examining the line widths, integrating the total area, and fitting the data with known spectra. Established numerical methods have been widely applied to extract spectral patterns in the presence of interfering compounds [e.g., Kramer, 1998; Morgan, 1991; Pelikan et al., 1994]. From our library of frequency scan data, numerical algorithms will be applied to produce a list of eigenspectra components for each unknown, composite spectrum. The library from which the eigenspectra are taken can be modified to account for the context of the measurement. The end result is a reconstruction of the unknown spectrum with a linear combination of library spectra weighted appropriately. Figure 8 is an example of a composite spectrum that can be deconvolved into components using a data set of spectra from end-members. This figure also shows that narrow lines can be extracted from a broad background signal, including ones that contain magnetic particles, such as maghemite and magnetite (likely constituents of martian soil).
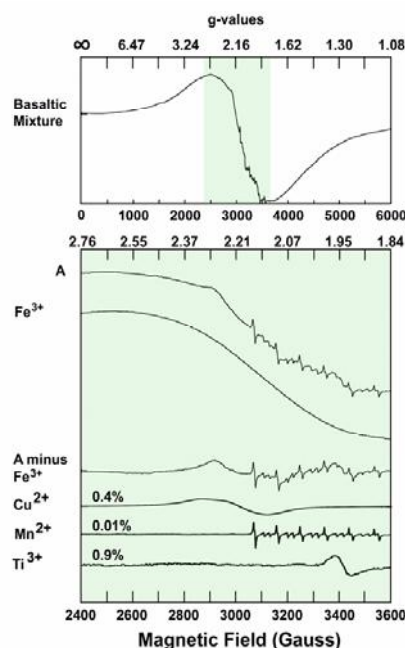

Figure 8: Composite spectrum of paramagnetic cations showing that the contributions of the individual constituents can be extracted.

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